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Performance of Ni-added Pd-Ag/Al_2O_3 catalysts in the selective hydrogenation of acetylene

Ji Hoon Lee*, Seok Ki Kim*, In Young Ahn*, Woo-Jae Kim, and Sang Heup Moon*,†**

*School of Chemical & Biological Engineering and Institute of Chemical Processes,
Seoul National University, Seoul 151-744, Korea
**Division of Energy and Biological Engineering, Kyungwon University, Gyeonggi-do 461-701, Korea

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Abstract−Effects of Ni addition on the performance of Pd-Ag/Al_2O_3 catalysts in the selective hydrogenation of acetylene were investigated. Ni-added Pd-Ag catalysts showed higher conversions than Ni-free Pd-Ag catalyst under hydrogen-deficient reaction conditions, hydrogen/acetylene <2.0, due to the spillover of hydrogen from reduced Ni to Pd and the suppression of hydrogen penetration into the Pd bulk phase, which enriched the Pd surface with hydrogen. Ethylene selectivity was also increased by Ni addition because the amounts of surface hydrogen originating from the Pd bulk phase, which was responsible for the full hydrogenation of ethylene to ethane, were decreased due to the presence of Ni at the sub-surface of Pd-Ag particles. Added Ni also modified the geometric nature of the Pd surface by blocking large ensembles of Pd into isolated ones, which eventually improved ethylene selectivity.

Key words: Acetylene Hydrogenation, Pd, Ag, Ni, Pd-hydride

INTRODUCTION

An ethylene stream obtained by naphtha cracking contains approximately 1% acetylene, which can easily deactivate the catalyst used for the subsequent polyethylene process. Therefore, the acetylene in the ethylene stream must be removed to a level of less than 5 ppm. Supported Pd-based catalysts are generally used for the hydrogenation of acetylene due to their high activity under mild conditions [1-3]. Previous studies have proposed a range of promoters, such as Ag, Cu, Ni, Ti and Si, to improve the performance of the Pd-based catalyst [4-9]. Among these candidate materials, Ag is widely used as a promoter in commercial catalysts.

Ag addition onto Pd improves ethylene selectivity and retards deactivation by providing electronic and geometric effects on Pd surface [4,10,11]. However, added Ag drastically decreases the activity of Pd-based catalyst because the amounts of surface active Pd sites are reduced due to the dilution of Pd surface by added Ag and also because the Pd surface is electronically modified by Pd-Ag alloy formation. Therefore, there is a limitation in improving the performance of Pd-based catalyst only by Ag addition.

The effect of Ni on the performance of Pd in hydrogenation of unsaturated hydrocarbons was investigated previously [12,13]. The Ni-promoted Pd showed a higher hydrogenation activity than Pd because the screening of active Pd by added Ni was minimized due to the segregation of Pd to the surface and because the intrinsic activity of Pd increased due to hydrogen enrichment on the surface [14,15].

In this study, Ni was added to the surface of Pd-Ag catalyst, and the performance of the Ni-added Pd-Ag catalysts was compared with that of Ni-free Pd-Ag catalyst. The surface of the prepared catalysts was analyzed by infrared spectra of CO adsorbed on the catalysts (CO-IR), temperature-programmed reduction (TPR) and the temperature-programmed desorption (TPD) of hydrogen from the catalyst.

EXPERIMENTAL

1. Catalyst Preparation

1 wt% Pd/Al_2O_3 was prepared by an incipient wetness method using $Pd(NH_3)_4(OH)_2$ as a Pd precursor and θ, δ-alumina (surface area=30 m^2/g, BASF) as a catalyst support. The prepared catalyst had a Pd dispersion of 25%, as estimated by H_2 chemisorption using ASAP 2010 (Micromeritics). To prepare Pd-Ag/Al_2O_3, Ag was added to 1 wt% Pd/Al_2O_3 by incipient wetness (atomic ratio of Ag/Pd=1) on 1 wt% Pd/Al_2O_3 using a solution of $AgNO_3$.

The Ni-promoted Pd-Ag catalyst was prepared by impregnating Pd-Ag/Al_2O_3 with a solution of $Ni(NO_3)_2\cdot6H_2O$. The Ni/Pd ratio of the catalyst was adjusted to 0.5, 1.0, 2.0 and 4.0 by using different concentrations of $Ni(NO_3)_2\cdot6H_2O$ in the impregnation solution. All prepared catalysts were finally dried at 110 °C overnight and calcined in air at 300 °C for 2 h.

2. Reaction Test

Acetylene hydrogenation was performed at 60 °C in a Pyrex microreactor containing 0.03 g of the catalyst. A gas mixture containing 1.1% acetylene in ethylene was used as a reactant stream. Prior to reaction tests, all catalysts were reduced at 150 °C for 1 h in flowing H_2 and N_2 (H_2/N_2=1). The reaction products were analyzed using an on-line G. C. (Agilent, model 6890N series with FID) equipped with a capillary column (HP-AL/S). The hydrogen/acetylene ratio (noted as H_2/Ac hereafter) was varied between 1.0 and 3.0 by changing the amounts of H_2 and N_2 in inlet stream while the total amount of reactant gas was fixed to 60 ml/min. Another set of reaction test was conducted at a fixed H_2/Ac ratio of 2.0. The flow rate of the reactant mixture was varied between 40 and 180 ml/min (space velocity=20,000-92,000 h^{-1}) to change the acetylene conversion.

3. Characterization

For CO-IR observations, sample catalyst in an amount of *ca* 0.07 g was pressed into a self-supporting disc and placed in an IR cell at-

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[†] To whom correspondence should be addressed.
E-mail: shmoon@surf.snu.ac.kr

tached with CaF_2 windows [16]. Prior to exposure to CO, the catalyst was reduced at 150 °C for 2 h in flowing H_2 and N_2 (H_2/N_2=1). The sample was exposed to 15 Torr of CO at room temperature for 5 min. IR spectra of adsorbed CO were recorded (Midac 2100) after gaseous CO had been removed from the cell by evacuation.

TPR experiments were conducted using a BELCAT analyzer. A 0.1 g of catalyst was introduced into a quartz reactor and heat-treated at 130 °C in Ar flow for 1 h to remove water from the sample. The catalyst was then cooled to room temperature, which was maintained 1 h prior to an increase to 500 °C in 5% H_2/Ar flow at a rate of 5 °C/min.

Prior to the TPD of H_2, a 0.1 g of sample was reduced at 150 °C in 5% H_2/Ar flow for 2 h. H_2 was injected onto the sample as pulses using a 1cc loop until the surface was saturated with H_2 at 30 °C. The sample was then purged with Ar for 1 h to be cleaned from weakly-adsorbed H_2. For TPD experiments, temperature was raised from 30 °C to 600 °C at a rate of 5 °C/min in an Ar flow.

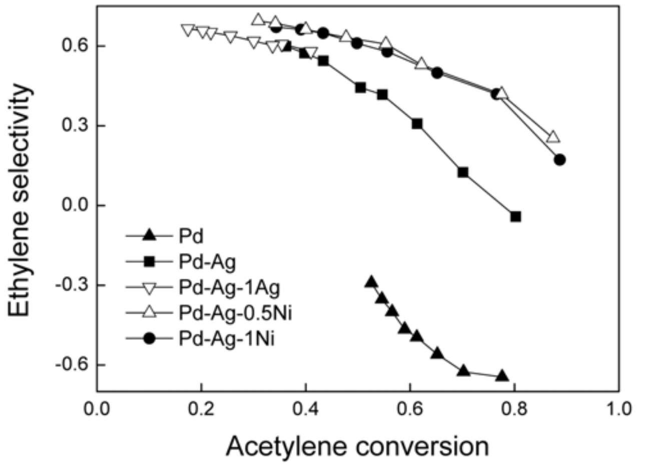

Fig. 2. Changes in ethylene selectivity with the conversion in acetylene hydrogenation on various catalysts.

RESULTS

1. Reaction Results

Fig. 1(a) shows acetylene conversions obtained using various catalysts at a fixed space time and at different H_2/Ac ratios. The acetylene conversion, which increased with an increase in the H_2/Ac ratio, was higher for Pd-Ag-0.5Ni and Pd-Ag-1Ni than for Pd-Ag catalyst, particularly when the H_2/Ac ratio was lower than 2.0. On the other hand, catalysts containing greater amounts of Ni, Pd-Ag-2Ni and Pd-Ag-4Ni, showed conversions similar to those for Pd-Ag catalyst at low H_2/Ac ratios, <2.0, and slightly lower conversions than the latter at the H_2/Ac ratio higher than 2.0. Ethylene selectivities obtained from the above experiments are presented in Fig. 1(b). The selectivity decreased with the conversion because ethylene was produced as an intermediate in the consecutive hydrogenation process [17]. Negative values of ethylene selectivity were obtained at high conversions because there was a net loss of ethylene due to the full hydrogenation of ethylene that had been contained in the feed stream. The ethylene selectivity, which was improved by Ni addition, was higher for catalysts containing larger amounts of Ni, Pd-Ag-2Ni and Pd-Ag-4Ni, than for the other cases, Pd-Ag-0.5Ni and Pd-Ag-1Ni.

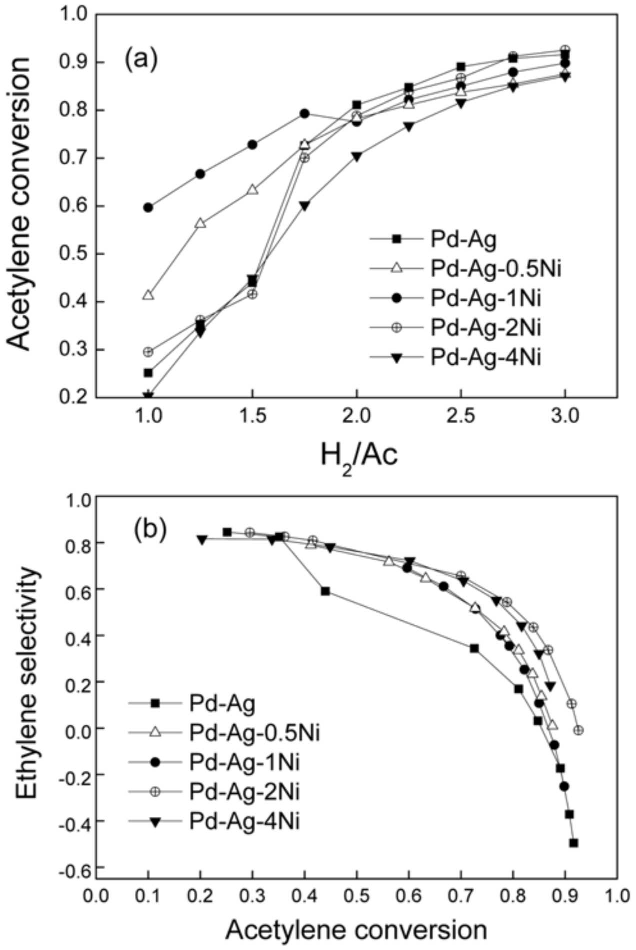

Fig. 1. Acetylene hydrogenation results obtained by changing the H_2/Ac ratio: (a) acetylene conversion, (b) ethylene selectivity at different conversions.

The reaction tests were also made by changing the flow rate of reaction gas at a fixed H_2/Ac ratio of 2, as shown in Fig. 2. Pd-Ag catalyst showed higher ethylene selectivity than Pd but the former was less active, showing lower conversions, than the latter. Pd-Ag-1Ag catalyst, which was prepared by impregnating Pd-Ag with additional amounts of Ag, was less active than Pd-Ag and its ethylene selectivity was similar to that of Pd-Ag. The Ni-promoted Pd-1.0Ag catalysts showed acetylene conversions similar to those of Pd-Ag catalyst, but ethylene selectivity was higher for the former catalyst than for the latter. In particular, ethylene selectivity obtained at high conversions was significantly improved by Ni addition.

2. CO-IR

Infrared spectra of CO adsorbed on the catalysts were observed (Fig. 3) to investigate the possible geometric modification of Pd by added Ni. Peaks observed at positions higher than 2,000 cm^{-1} represent the CO species that are linearly bound to the surface Pd sites, and those at 2,000-1,800 cm^{-1} are assigned to the multi-bound CO species [18]. When Ni was added to the catalysts, peaks representing the multi-bound CO species were reduced in the intensity, and simultaneously those representing the linearly-bound CO species were slightly intensified. As a result, the area ratio of the peaks for

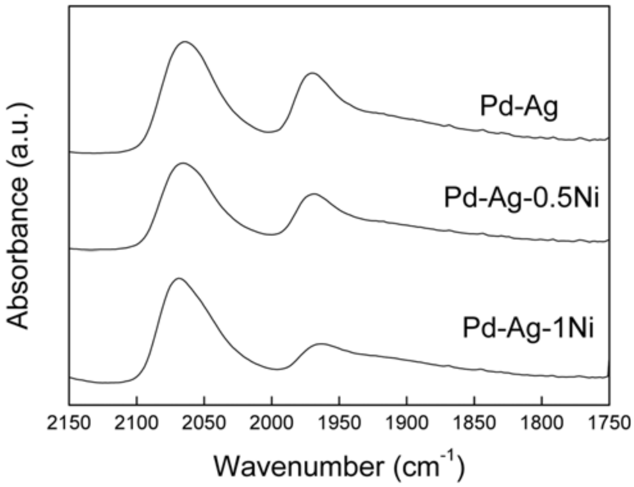

Fig. 3. FT-IR spectra of CO adsorbed on various catalysts.

Table 1. The intensity ratio of a linear-bound CO peak (A_l) to a multi-bound CO peak (A_m), estimated from CO-IR for Pd-Ag and Pd-Ag-xNi

Catalyst	Linear/Multi
Pd-Ag	1.2
Pd-Ag-0.5Ni	1.4
Pod-Ag-1Ni	1.8

the linearly-bound CO and for the multi-bound CO species (A_l/A_m) was increased by the Ni addition, as summarized in Table 1. The above results indicate that large Pd ensembles that were responsible for the adsorption of the multi-bound CO species were blocked by added Ni species, which simultaneously converted the large Pd ensembles to isolated Pd sites that adsorb CO in a linearly-bound mode [19].

3. TPR and Hydrogen TPD

TPR results of a few sample catalysts are presented in Fig. 4. Pd-Ag was observed to be reduced at temperatures lower than 100 °C. On the other hand, Ni/Al_2O_3 started to be reduced at 200 °C and was completely reduced at 330 °C. It is noteworthy that the reduction of Pd-Ag-1Ni catalyst was completed at 120 °C, which was lower than the temperature used for the pre-reduction of catalysts prior to reaction tests in this study. According to previous reports, the reduction temperature of NiO was lowered in the presence of Pd due to hydrogen spillover from Pd to NiO [20, 21].

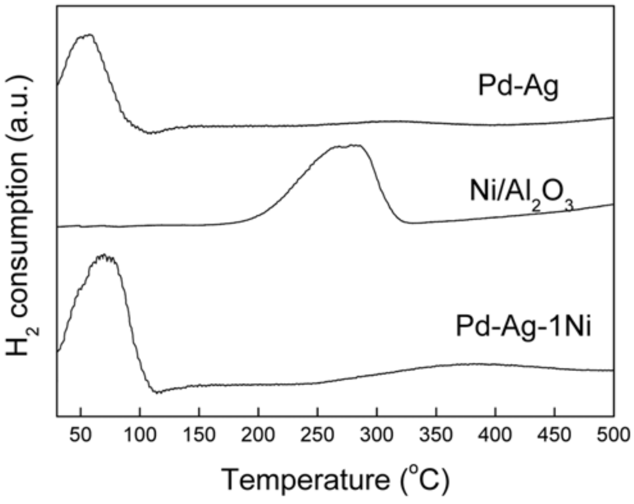

Fig. 4. Changes in the TCD signal during the temperature-programmed reduction of various catalysts.

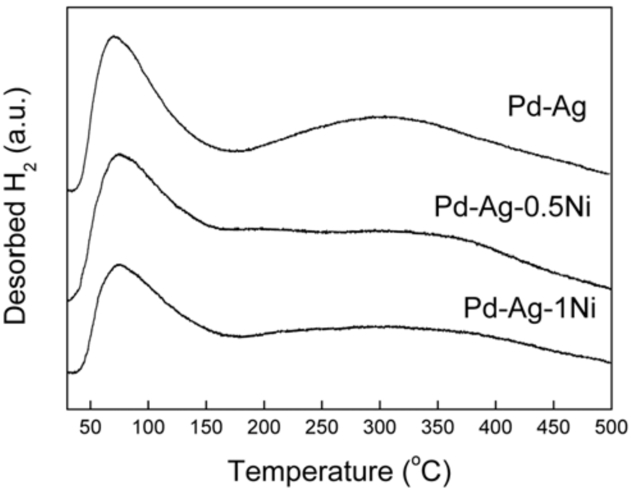

Fig. 5. Changes in the TCD signal during the temperature-programmed desorption of hydrogen from various catalysts.

Fig. 5 shows the TPD of hydrogen from various catalysts. Peaks observed at temperatures lower than 180 °C represented hydrogen desorption from the catalyst surface and those above 180 °C were due to hydrogen from a Pd bulk phase [22,23]. The amounts of hydrogen from the Pd bulk phase were significantly decreased and consequently the ratio of surface to bulk hydrogen increased in the Ni-added catalyst.

DISCUSSIONS

1. Catalytic Activity

Fig. 2 indicated that the catalytic activity for acetylene conversion decreased in parallel with the amounts of added Ag, which originated from the dilution of Pd active sites by added Ag [11,24]. On the other hand, the activity was not decreased by Ni addition onto Pd-Ag catalyst, and instead increased to certain extents particularly at low H_2/Ac ratios (Figs. 1(a) and 2). We confirmed by separate experiments that catalyst containing only Ni showed negligible hydrogenation activity under the reaction condition of this study.

The unchanged or increased activity of Ni-containing Pd-Ag catalysts can be explained based on two factors described below. One factor is that Ni added to Pd-Ag was completely reduced at low temperatures, below 120 °C, as indicated by Fig. 4. Therefore, Ni can work as an additional source of hydrogen that eventually migrates onto Pd or support [25,26]. Hydrogen adsorbed on Pd is not only used for the hydrogenation of acetylene but penetrates into the Pd bulk phase to form Pd β-hydride and spillover to support as well [4,27]. As shown in the hydrogen-TPD results (Fig. 5), Ni addition to Pd-Ag decreased the amounts of hydrogen desorbing from the

Pd bulk phase. Previous researches on Pd and Ni alloy reported that Pd segregated to the surface of the bi-metallic particle due to the lower surface tension and larger atomic radius of Pd compared with those of Ni [12,13]. Accordingly, the other factor related to the role of Ni was that a fraction of added Ni was located at the sub-surface of Pd-Ag particles, thus preventing the penetration of hydrogen to the Pd bulk phase and eventually making the Pd surface rich in hydrogen. In addition, the blockage of Pd active sites by added Ni can be minimized due to the segregation of Pd to the surface.

In summary, the origin of relatively high activity of Ni-added catalysts can be explained by two factors: supply of extra hydrogen from reduced Ni to Pd and the blockage of hydrogen penetration to the Pd bulk phase due to the presence of Ni at the sub-surface of Pd.

2. Improved Ethylene Selectivity

Figs. 1(b) and 2 clearly demonstrate that ethylene selectivity was increased by Ni addition onto Pd-Ag, which can be explained as follows. The major adsorption modes of ethylene on Pd are known to be π-bonded and di-σ-bonded ones [28]. π-Bonded ethylene species are adsorbed on single Pd atoms and easily desorbed as ethylene because the adsorption strength is relatively weak. On the other hand, di-σ-bonded ethylene species, which are strongly bound to Pd, require two or more neighboring Pd atoms and are likely to be fully hydrogenated to ethane, thus lowering ethylene selectivity. According to Fig. 3 and Table 1, the intensity ratio of IR peaks representing linearly-bound CO and multi-bound CO (A_l/A_m) was increased by Ni addition, which indicated that added Ni blocked large Pd ensembles into smaller ones [27]. Because the linearly-bound CO species represent isolated surface Pd atoms, the above IR results indicate that ethylene has a better chance to be adsorbed as π-bonded species, thus contributing to ethylene selectivity, on the Ni-added catalysts.

The other reason for the improved ethylene selectivity on Ni-containing catalyst is the following. As mentioned in section 4.1 concerning the activity of Pd catalyst, hydrogen in the Pd bulk phase (β-hydride) is more active than hydrogen on the Pd surface and therefore is detrimental to ethylene selectivity [27]. Because the amounts of hydrogen in the Pd bulk phase (β-hydride) were reduced by Ni addition (Fig. 5), Ni-containing catalysts show higher ethylene selectivity than Ni-free ones.

CONCLUSIONS

Ni-promoted Pd-Ag catalysts showed higher ethylene selectivity than Ni-free ones, but the catalytic activity remained nearly unaffected by Ni addition except under the reaction condition of low H_2/Ac ratio, <2.0. Reasons for the high ethylene selectivity of Ni-promoted catalysts were an increase in the amounts of isolated surface Pd atoms due to the blocking of large Pd ensembles by added Ni and the suppression of active hydrogen (β-hydride) originating from the Pd bulk phase. The activity of Ni-containing catalyst was higher than that of Ni-free one at low H_2/Ac ratios because added Ni provided additional hydrogen to Pd and also because added Ni suppressed the penetration of hydrogen into the Pd bulk phase, such that the Pd surface remained rich in hydrogen.

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